A procedure for identifying possible products in the Assembly-Disassembly-Organisation-Reassembly (ADOR) synthesis of zeolites

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High silica zeolites are some of the most important and widely used catalysts in modern industry, and they have potential for application across a wide range of traditional and emerging technologies. The many different structural topologies available to zeolites open up many different potential uses so there is still a strong drive to prepare new zeolites. Here we present a protocol for a relatively new method of preparing these important solids called the Assembly-Disassembly-Organization-Reassembly (ADOR) process. It allows for the synthesis of new high silica zeolites that are thought to be unfeasible through traditional methods, opening up new topologies that may find new industrial applications. A procedure for identifying the optimum conditions (time of reaction, temperature, acidity etc.) for the ADOR process has been developed. The ADOR method is a complex process with different possible outcomes. Following the protocol will allow researchers to identify the different products that are possible from the reaction without recourse to repetitive and time-consuming trial and error. In developing the protocol, germanium-containing UTL zeolites were subjected to hydrolysis conditions using both water and hydrochloric acid as media, which provides an understanding of the effects of temperature and pH on the Disassembly (D) and Organization (O) steps of the process that define the potential products. Samples were taken from the ongoing reaction periodically over a minimum time of 8 hr and each sample was analysed by powder X-ray diffraction to yield a time course for the reaction at each set of conditions, with selected samples analysed by transmission electron microscopy and solid-state NMR spectroscopy.

INTRODUCTION

Zeolites are an important class of microporous solids that are widely used in industry. They are one of the most important families of heterogeneous catalysts in use today,[1,2] but are also used in a wide variety of other applications from ion exchange and water softening, through to medical applications. The Assembly-Disassembly-Organization-Reassembly (ADOR) process[3–9] is a new method for preparing members of this important class of compound. This differs from traditional zeolite synthetic processes, which generally involve reversible crystallization under hydrothermal conditions,[10] followed by an irreversible condensation to form the final framework.[11] The consequence of this is that materials with unexpected energetic properties can be prepared using ADOR that are unlikely to be possible using the traditional methods.[3]

Table 1. Differences in preparation of high silica zeolites. Advantages are colour coded blue. Limitations are colour coded red. Advantages are marked with an asterisk.

Method / ***Factor***	***Hydrothermal crystallisation***	***ADOR***
Controllability and predictability of products	Limited control and the product zeolite is not always easy to predict	*Use of layers as predefined building unit leads to product being predictable
Diversity of products	Synthesised zeolite may be limited by the reversible nature of crystallisation step	*No inherent limitation on the types of products possible
Chemical composition	*Zeolites can be prepared using a wide variety composition of reaction mixture	So far limited to the germanosilicates as parent materials
Price	Often (but not always) needs expensive organic structure directing agents	Use of expensive germanium in parent materials

This opens up the possibility of preparing materials with different structures than those currently possible, which in turn may lead to new applications. There are many advantages and limitations to using both traditional hydrothermal synthesis and the ADOR process. Just a few of these have been highlighted below in Table 1.

A key feature required for the success of the ADOR method is the structure and chemistry of the parent zeolite that is assembled in the first step of the process, usually following previous literature methods. Research so far has concentrated on parents that have silica-rich layers linked by germanium-rich cubic units, termed double four rings (d4rs).[12–16] Generally, to be successful in the ADOR process, these d4r units must contain enough Ge to break the connections between the layers as the Ge is hydrolysed, allowing the parent zeolite to be disassembled.[17,18] The specific location of the Ge within the d4r units is often difficult to determine without highly specialised diffraction experiments.[17] There are several known zeolite topologies that have the features necessary for successful application in the ADOR process. These include **UTL**,[3,6,7] **ITH**,[19] **ITR**,[19] **IWR**,[19] **IWW**,[20] **UOV**[21,22] and the recently discovered SAZ-1[23] (note that a description of how the nomenclature of zeolites is derived is found below). There are several characterisation techniques that have been used to probe the ADOR mechanism and the daughter zeolites produced, including powder X-ray diffraction (PXRD) and the subsequent Rietveld refinement,[24,25] *in situ* and *ex situ* Pair Distribution Function (PDF) analysis,[24,26] solid-state NMR spectroscopy[25,27] and high resolution electron microscopy.[5,16]

The ADOR process is extremely flexible, and starting from only one parent zeolite with the **UTL** framework topology a family of six new zeolites, named IPC-2 (**OKO**), IPC-4 (**PCR**), IPC-6 (***PCS**), IPC-7, IPC-9 and IPC-10, can be prepared.[3,6,7] Previously reported by Wheatley *et al*.,[5] a study showed the pH dependence of hydrolysis and subsequent rearrangement. It was found that the rate of the initial hydrolysis (disassembly) does not depend greatly on the pH of the hydrolysis medium. Unlike the hydrolysis however, the rearrangement process is influenced by the acidity of the reaction media. When HCl of < 0.1 M is used, IPC-4 (**PCR**) is formed preferentially after reassembly; increasing the molarity shows a steady increase in inter-layer spacing, and materials such as IPC-6 (***PCS**) can be formed. When the acidity is high enough, all reactions formed IPC-2 (**OKO**). [5] Time is also an important variable in the reaction outcome.

Such diversity of outcomes points to a complex mechanism that must be understood in detail if the full potential of the process is to be realised. The different outcomes depend on the conditions used, and it is therefore very easy to miss prospective products by not surveying the potential conditions over a sufficient range. To avoid this possibility, we have developed a standard protocol through which a wide range of conditions are tested. Here we present this protocol using zeolite **UTL** as an archetypal parent zeolite.

Design and overview of the procedure

The ADOR process (Figure 1) has four main steps: formation of the pre-determined parent zeolite containing the required properties (Assembly); regioselective removal of the Ge-rich d4r by exploiting the

chemical weakness within to produce a layered species (Disassembly); an organization (rearrangement/re-intercalation) step where the layers are brought into the correct orientation for reconnection (Organization); formation of new Si-O-Si bonds between the layers to produce new daughter zeolites after subsequent calcination (Reassembly).[7]

The procedure presented here concentrates on identifying the intermediates that result from the D and O stages in the process, as it is these stages that really control the nature of the final product. There are three main variables that have to be controlled: time, temperature, and acidity of the disassembly medium. If all possible outcomes from the ADOR process are to be recognized it is important that sufficient parameter space is sampled. On the other hand, we want to make sure that the protocol is efficient in terms of time. By considering this balance, we have designed a protocol that uses four different disassembly media (water, 0.1 M HCl, 1.5 M HCl, and 6M HCl) and temperatures that range between 20 and 100 °C. It is also important to develop a simple method to systematically monitor the progress of the ADOR process as it proceeds. As the samples taken during the course of the reaction are crystalline (or semi-crystalline) PXRD is an appropriate tool to study samples that are recovered from the reaction as it progresses. In particular, the d spacing at which the *200* reflection appears in the XRD pattern gives an excellent indication of the interlayer spacing in the material. The d_{200} value can then be plotted against time for each of the chosen conditions (temperature and acidity) to yield plots that are instructive in determining how the reaction is proceeding, and allowing us to identify the various steps in the process. Other techniques, such as solid-state NMR spectroscopy and high-resolution transmission electron microscopy (HRTEM) can then be used as required to further characterize different samples.

The starting point for the protocol developed here uses water as the disassembly (hydrolysis) medium and the reaction is completed under reflux. The equipment is assembled as shown in Figure 2 and as described in detail below. A three-neck round-bottom flask is charged with the hydrolysis medium, and the system brought to the required temperature. The parent zeolite is added to the system and samples of the solid material in the reaction are taken at specified time intervals. These samples are analysed using PXRD. The conditions used for the procedure can then be altered as required to find all possible products as demonstrated below.

Extensions

While this protocol uses only Ge-**UTL** as the parent zeolite, it is designed so that any parent zeolite can be substituted in its place. This will be particularly useful as new parent zeolites are discovered, as the protocol will provide evidence rapidly as to whether the ADOR process can be successfully applied or not.

Limitations

Given the knowledge of the ADOR process at the present time it is likely that this protocol will provide detailed information on the disassembly stage of the process, as this generally happens quickly and at low temperature. However, for parent zeolites other than **UTL** the reintercalation/rearrangement step might not occur at a rate that can be probed by this protocol on a sensible timescale. If higher temperatures are required then a new experimental set up, using hydrothermal equipment, may be necessary.

Terminology

Unlike many organic or inorganic compounds, zeolites and zeo-types cannot be named by classic naming methods. Instead, the material is named for the establishment where it was first produced and then given a 3-letter code once accepted into the International Zeolite Association (IZA) database. For example, IPC-4 was named as the Institute of Physical Chemistry zeolite 4, and then, upon acceptance by the IZA database, was given the code **PCR**. The archetype parent zeolite, **UTL**, discussed in this protocol was produced by 2 groups in 2004. It was given the name IM-12 (Institut Français du Pétrole/Mulhouse-12)[28] by Paillaud *et al.* and ITQ-15 (Instituto de Tecnología Química-15)[29] by Corma *et al.* and assigned the IZA code **UTL**. The addition of an asterisk to the IZA code (such as in ***PCS**) indicates that there is some disorder in the characterised material. Further information on nomenclature can be found on the IZA website, www.iza-online.org.

To differentiate between the final products that are produced after the reassembly (R) step from the precursors that are formed only after the disassembly (D) and organisation (O) steps, the latter are given an extra P in their names. For example, IPC-2P is the precursor that is formed after the D and O steps (Figure 1); after the reassembly step this will form the fully connected zeolite IPC-2.

Table 2. Terminology for the daughter zeolites discussed in-depth throughout this manuscript. All zeolites discussed are produced from Ge-**UTL**.

Precursors formed before final reassembly step	*Calcined final zeolite*	*IZA Code for final zeolite*	*Structure between silicate layers of calcined zeolite*
IPC-1P	IPC-4	**PCR**	Direct oxygen linkages
IPC-2P	IPC-2	**OKO**	Single-four-rings (s4r)
IPC-6P	IPC-6	***PCS**	Alternate layers of direct oxygen linkages and s4r

MATERIALS

As far as meaningful, please check that you have inserted relevant suppliers and catalog numbers.

REAGENTS

CAUTION Hydrochloric acid used in the hydrolysis is corrosive. Consult the material safety data sheets for each item. All suitable personal protection equipment (PPE) should be worn: safety glasses, appropriate gloves and laboratory coat. All experimental work should be carried out in a fume hood.

- Hydrochloric acid; 12, 6, 1.5, 0.1 M (Fisher, 37%, LOT: 1713904, Code: H/1200/PB17)
- De-ionised water
- Ge-**UTL** (see refs. 3 + 19)

EQUIPMENT

- Three-necked round-bottom flask, 250 mL
- Weighing balance (Sartorius)
- Water condenser
- Stirrer bar
- Heating mantle

- Glass pipettes
- Watch glass (x 5)
- Thermometer
- Powder funnel
- Glass funnel
- Ceramic Buchner funnel
- Buchner flask, 100 mL
- Filter seal vac-ring, neoprene rubber
- Filter paper
- Glass vials
- Measuring cylinder
- Drying oven
- Weighing paper
- Mortar and pestle
- Borosilicate capillaries, 0.5 mm
- Forceps
- Spatula
- Carbolite 2416 Tube Furnace for calcination
- STOE STADIP operated in capillary Debye-Scherrer mode, operating Cu $K_{\alpha 1}$ radiation
- Bruker Avance III spectrometer, equipped with a 9.4 T wide-bore superconducting magnet (solid-state NMR spectroscopy)
- Jeol JEM 2011 (HRTEM)

PROCEDURE

Preparation of parent zeolite (using Ge-UTL as an example)

TIMING 12 days

NOTE Any suitable parent zeolite can be substituted for Ge-**UTL**. Synthetic procedures from previous literature can be used for known zeolites.

1. Prepare parent Ge-**UTL** with molar composition 0.8 SiO_2: 0.4 GeO_2: 0.4 ROH: 30 H_2O according to well-known literature procedure.[3,26]

   TROUBLESHOOTING

2. Remove the SDA from Ge-**UTL** by calcination of the as-synthesized zeolite in a stream of air at 575 °C for 7 hr with a temperature ramp (uphill) of 1 °C min^{-1}, plateau for 6 hr, and then a temperature

ramp (downhill) of 2 °C min^{-1} until room temperature is reached. To prevent accidental disassembly by moisture in the air the sample can be stored in. a desiccator to keep it dry.

<PAUSE POINT> The sample can be stored in a desiccator for up to….xxx days?

TROUBLESHOOTING

Set-up of hydrolysis apparatus

TIMING 1 hr

3. Equip the three-necked round-bottom flask with the condenser and attach to the water.
4. Place the three-necked round-bottom flask in heating mantle with stirrer bar.
5. Add 120 mL water into the three-necked flask. Heat the water to 100 °C and stir at a speed of 600 rpm.

   CRITICAL to ensure that the liquid in the experiment remains at the required temperature the heating mantle may need to be set at a higher temperature. Check that the temperature of the liquid is at 100 °C throughout the experiment.
6. Set up the filtration apparatus by way of Buchner flask, funnel and ring. Attach the flask to the water vacuum pump.
7. Prepare pipettes, pipette teats, glass vials, and capillaries for each aliquot taken (ca. 30). Name each vial by the time the sample is taken.

   CRITICAL STEP Prepare all of this glassware before moving on to step 8, because….
8. Weigh out 600 mg of Ge-**UTL** and grind to a fine powder in the pestle and mortar. The crystallite size at the end of this process is, on average, about 10 μm × 10 μm × 3 μm as measured by scanning electron microscopy.

Hydrolysis procedure

TIMING 8hr

9. Add the ground Ge-**UTL** to the three-necked round-bottom flask with stirring and start the timer.
10. After 1 min take the first sample (ca. 4 pipettes full, ensuring that solid is present in the sample; c.a. 2.5 to 3 mL of suspension), filter for 50 sec and transfer to a labelled watch glass and place in a drying oven for 5 min at 80 °C.

11. Repeat step 10 every 1 min up to the 5 min mark.

12. After the 5 min mark continue to take samples every 5 min up to 1 hr. Filter each sample taken for 4 min and dry at 80 ° C for 5 min.

TROUBLESHOOTING

13. After 1 hr, continue to take samples every 30 min up to 8 hr (or when the reaction has come to completion). Filter each sample for 5 min and dry in the drying oven at 80 °C for 5 min.

14. Follow steps 10 – 13. After each subsequent drying of a sample, remove from the oven and grind in mortar and pestle until fine.

15. Pack the hydrolysed material in 0.5 mm borosilicate capillaries until half full.

PAUSE POINT Vials containing the capillaries can be sealed with a screw cap and placed in a vacuum desiccator for up to 2 weeks.

TROUBLESHOOTING

General procedure for zeolite characterisation

16. We have included procedures for collecting PXRD (option A), solid-state NMR spectroscopy (option B) and TEM (option C). Procedures include the characterisation of PXRD (option D).

(A) Procedure for collecting PXRD data **TIMING 1 hr per sample**

(i) Pack the hydrolysed material in a 0.5 mm capillary. Using forceps to vibrate the material down the capillary.

(ii) Collect PSRD data using a STOE STADIP powder X-ray diffractometer operated in Debye-Scherrer mode, using a scintillation position-sensitive linear detector, operating CuK α_1 radiation, place the capillary in the holder and centre into the middle of the beam using a microscope. Scan the diffraction pattern for 55 min between 3° and 40° 2Θ with a step size of 0.2°

(B) Procedure for preparing and collecting samples for solid-state NMR spectroscopy
TIMING 24 hr per sample

(i) Using a Bruker Advance III spectrometer equipped with a 9.4 T wide-bore superconducting magnet, at a Larmor frequency of 79.459 MHz, collect ^{29}Si solid-state NMR spectra.

(ii) Pack samples into 4 mm ZrO_2 rotors and rotate at a MAS rate of 10 kHz. Weigh rotors before and after packing to determine the mass of zeolite used in the acquisition.

(iii) Using a radiofrequency (rf) field strength of ~83 kHz, with a recycle interval of 120 s, collect magic angle spinning (MAS) spectra.

(iv) Determine the Q^3:Q^4 ratio using DMFit (or other suitable program),[30] with errors estimated from multiple fits.

The commercial probe used does not display a ^{29}Si background signal hence no correction has to be made to the absolute Q^3:Q^4 ratios plotted to reflect this.

(v) Show the chemical shifts relative to TMS (using secondary references of Q^8M^8 ($\delta(OSi(OMe)_3)$ = 11.5 ppm) for ^{29}Si and L-alanine ($C_3H_7NO_2$ (δ (NH_2) = 8.5 ppm) for ^1H).

(C) Procedure for preparing and collecting samples for TEM

TIMING 1 hr per sample

(i) Grind the powder sample in mortar with pestle.

CAUTION Germanosilicates are extremely sensitive to the electron beam, care must be taken during the sample preparation and imaging. To avoid sorption of water, samples must be dried in an oven and stored in a vacuum desiccator.

(ii) Add acetone to ground powder, grind again to obtain a well dispersed suspension of zeolite crystals in acetone.

(iii) Using a pipette, place one drop of suspension on the copper/holey carbon TEM grid.

(iv) Calibrate the microscope using standard gold film method.

(v) Image the samples of silicates using HRTEM method. Use minimum electron beam intensity due to instability of samples. Use spot size 3 and gun lens 3. In our lab, high-resolution transmission electron microscopy (HRTEM) is performed using a Jeol JEM-2011 electron microscope. If you are using this equipment, set the accelerating voltage of 200 kV.

<CRITICAL STEP> Make sure to spread the beam to reduce the intensity, keeping the beam intensity below 2 pA cm^{-2}.

(vi) Recorde the HRTEM images. In our lab we use a 9 Gatan 794 CCD camera. Calibrate the camera length, sample position and magnification using standard gold film methods.

(vii) Analyse recorded samples by ImageJ program generating the FFT patterns and calculating the d spacings from generated diffraction patterns.

(D) Procedure for analysing PXRD data

(i) Locate the *200* reflection in the PXRD pattern and measure its position as accurately as possible (this is usually best achieved using the fitting program that comes as part of the standard diffractometer software, but could be performed using other software packages equally successfully). The *200* reflection is normally the most intense peak in the pattern, but this can be confirmed by calculating the positions of the reflections using the expected unit cells.

CRITICAL STEP The *200* peak is chosen here, because it corresponds to the interlayer spacing for UTL. For other parent zeolites, the orientation of the reported unit cell may mean that the interlayer distance is defined using a different reflection. The appropriate reflection must be chosen in this stage otherwise results may be incorrect.

CRITICAL STEP The 200 peak may be relatively wide during the hydrolysis step due to a mixture of interlayer connectivity in the material, which means the the measurement may be difficult and the error associated with measuring the position of such peaks should be taken into account.

(ii) Calculate d-spacing of the *200* peak using the Bragg equation (if your fitting software does not do this automatically for you). This gives the d_{200} peak in Å, and is a direct probe of the layer spacing in the material.

(iii) Plot d_{200} against time for all data sets. If the *200* reflection moves significantly during the process then this is an important indicator of whether the parent material is susceptible to the ADOR process. The movement of the peak gives an indication of the types of intermediate that are accessible under the conditions of study; this should be usedto monitor (a) the effect of temperature and (b) the effect of pH.

TIMING

Step 1-2: 12 days

Steps 3-8: 1 hr

Steps 9-11: 5 min

Step 12: 55 min

Step 13: 7 hr

Steps 14-15: 5 min

TROUBLESHOOTING

Trouble shooting guidelines can be found in Table 3.

Table 3. Troubleshooting Table

STEP	*PROBLEM*	*POSSIBLE REASON*	*SOLUTION*
1	Parent zeolite not crystalline or not of the correct structure	Parent material did not form correctly in the assembly step.	Check the PXRD to make sure the pattern is correct. If pattern does not match that for expected parent zeolite then repeat synthesis of parent material.
2	The parent is amorphous after calcination (by PXRD)	The parent has degraded in the calcination process	Analyse the calcined material PXRD and check material by ^{13}C NMR to detect SDA presence; Repeat calcination with fresh parent zeolite following calcination steps at the correct temperature. This step can vary with different equipment so several attempts may be required.
12	Hydrolysis (disassembly) did not occur	Ge is not regioselectively incorporated; Low amount of Ge in sample – not enough to remove d4r; Too much Ge – XRD shows no peaks suggesting a collapse of the layers	Perform ICP or other elemental analysis to ascertain Si:Ge ratio in material; re-synthesise parent zeolite with better control of Si:Ge ratio
12	Hydrolysis not efficient over a sensible time scale	Disassembly of the interlayer linkages did not occur, perhaps due to large numbers of stacking faults in the material.	Analyse by scanning electron microscopy to look at morphology and HRTEM to detect faulting; Preparation of parent zeolite without intergrowths

15	No evidence of separate rearrangement steps in the reaction profile.	The D and O steps may be overlapping dependent on hydrolysis media used. The induction step has not occurred as the material has not fully hydrolysed before starting to rearrange; this could be a real effect dependent on the parent zeolite used	Take samples over a longer timeframe to determine whether rearrangement will occur or whether the layered material is the only daughter zeolite formed

ANTICIPATED RESULTS

Reaction in water at 100 ºC As described above, samples of the solid in the reaction are taken at regular intervals from the reaction and PXRD patterns measured for each sample. Figure 3 shows selected PXRD patterns, and the inset shows how the position of the *200* reflection varies with time during the reaction. The patterns chosen correspond to the three main intermediates in the ADOR process for Ge-**UTL**: IPC-1P, IPC-2P and IPC-6P. Figure 4 shows a plot of the time dependency of the d-spacing of the *200* reflection for all the samples. The plot shows that the parent Ge-**UTL** zeolite (d_{200} = 14.48 Å) is quickly disassembled (hydrolysis and removal of the Ge-rich d4r units) leading to a contraction of the interlayer distance. After approximately 30 minutes the value of d_{200} levels off at 10.5 Å, which corresponds to the IPC-1P intermediate (Figure 1) where all the d4r units have been removed from between the layers. At first sight one might imagine that the reaction might have concluded at this time. However, the importance of following the procedure for a significant time is obvious as at longer times further changes occur. There is an induction period, during which IPC-1P is the only product identified in the reaction. After 120 minutes (under these conditions) the d_{200} value increases once again until it plateaus at a value of ~11.75 Å, which corresponds to IPC-2P (Figure 1), where some extra silicon has been incorporated back into the interlayer space through a reintercalation/reorganisation reaction. Following this protocol also allows one to identify the time at the mid-point in the reintercalation process. This is the intermediate IPC-6P, which is the material where half of the layers have undergone the intercalation and half have not. This is a very unusual structure that is fully described in reference 18.

The Avrami-Erofeev model[22] can be employed to model the solid-state kinetics for the hydrolysis (D) and rearrangement (O) steps. To do this the extent of reaction, α is plotted against time, and the Avrami-Erofeev equation fitted to give the Avrami exponent, n and the rate constant k for each step at each temperature probed. Figure 5 shows the plots for the D and O steps at 100 ˚C. These plots can be repeated at

all temperatures to gain further insight in to the reaction kinetics; however, such analysis is beyond the scope of this protocol.

Solid-state NMR spectroscopy and TEM

The products of the hydrolysis and rearrangement steps for Ge-**UTL** at 100 ºC were further analysed by solid-state NMR spectroscopy and TEM. Samples were taken when major structural changes had taken place: 1 hr (IPC-1P), 4 & 8 hr (both IPC-2P). Using ^{29}Si MAS NMR spectroscopy, the change in both Q^4 ($Si(OSi)_4$) and Q^3 ($Si(OSi)_3(OH)$) species can be monitored over time (Figure 6). The growth of the Q^3 peak after 1 hr, suggests the formation of silanol (Si-OH) groups in the layered species, IPC-1P. After 1 hr the Q^3 peak reduces in intensity as they rearrange to Q^4 sites in accordance with Figure 1.

After an initial hydrolysis at 1 hr, the ratio of Q^3:Q^4 sites is 1:2.3, thus close to the ideal ratio of 1:2.5 for IPC-1P. The Q^3:Q^4 ratio continues to decrease as the rearrangement process occurs, leading to a ratio of 1:4.8 upon formation of IPC-2P at 4 hr (ideal IPC-2P Q^3:Q^4 = 1:7). Due to the relative difference between actual and ideal ratios, we can conclude that some silanol groups remain as defects throughout the material.
TEM images for the two most important samples (1 hr, and 4 hr) highlighted by XRD were recorded. These materials are highly unstable during radiation. However, the TEM images highlight some loss of crystallinity from parent Ge-**UTL** over the course of 1 min (Fig. 7. ESI) and a clear drop in d spacing can be seen over the first hr (IPC-1P), before this increases again to form IPC-2P. The results corroborate those from the XRD data.

The Effect of Temperature

The hydrolysis and rearrangement mechanisms of Ge-**UTL** through the ADOR process were investigated over a period of 8 hr using water as the hydrolysis medium at six different temperatures (100, 92, 85, 81, 77 and 70 ºC). Figure 7 shows the change in d spacing with time for all these temperatures. The initial hydrolysis occurs rapidly over the course of 1 hr and several features can immediately be identified. First, it is clear that the initial Disassembly is fast under all conditions. Indeed, it is so fast that the errors associated in accurate measurement of the time are likely to be significant, and limit any quantitative conclusions that can be elucidated from the data for this process (at least using this protocol). Second, the duration of the induction period varies greatly with temperature; as the temperature of the reaction is lowered the induction period increases in length. Third, the rate of the reintercalation/reorganisation step increases with temperature. Clearly, there is the possibly of quantifying reaction rates and apparent activation energies using these data, but this is beyond the scope of this protocol paper. However, the data does give excellent qualitative information that helps to show which particular set of conditions might be the optimum for the preparation of the desired product, IPC-1P, IPC-6P or IPC-2P.

The Effect of pH

The hydrolysis and rearrangement mechanisms of Ge-**UTL** were further investigated by varying the concentration of hydrochloric acid (6, 1.5 and 0.1 M). The temperature was kept constant at 20 ºC to ensure only the effect of acid strength was monitored (Figure 8).

The reactions undertaken in strong acid (6 M) were rapid, with both the hydrolysis and rearrangement occurring almost simultaneously. In other words, the induction period is reduced to zero and the disassembly never has time to complete before rearrangement occurs and only IPC-2P is formed under these conditions. In 1.5 and 0.1 M HCl, the reaction is much slower and a full hydrolysis to IPC-1P can be seen, much more similar to that seen in water.

Extension of the protocol to other parent zeolites and subsequent troubleshooting

The above protocol has been designed with UTL as the parent zeolite topology and will allow researchers to synthesise the previously prepared materials listed above. However, perhaps the most important aspect of the protocol is the framework it provides for the testing of potential new parent zeolites. When a researcher has a parent material with the structural features that may make it appropriate as a starting point for the ADOR process, following the above protocol will provide solid evidence for whether the material is suitable or not. In the ideal circumstance one would know the crystal structure of any parent before embarking on a study using this protocol. However, even if one does not yet know the detailed structure, noting that a major PXRD diffraction peak changes position during the protocol may well indicate that the parent has promise and may provide helpful clues as to the possible structure of the parent.

Substituting a new parent zeolite for the UTL in the protocol is the simplest approach, but there are clearly potential pitfalls to this and the process is unlikely to work in exactly the same manner for all parent zeolites. Nevertheless, by examining how the protocol differs can provide valuable information on the parent zeolite as well as any ADOR intermediates that may be formed. There are a few steps where we anticipate that some troubleshooting intervention or optimisation would be required in order to get meaningful results.

Disassembly: The first potential problem that may occur is that the disassembly step does not work as expected. If the d_{200} reflection remains unchanged, this indicates that there is likely not enough Ge in the structure to enable successful disassembly. The appropriate course of action would therefore be to prepare the parent with an increased Ge content and repeat the protocol. At the other extreme, the PXRD patterns collected after the hydrolysis may show significant deterioration to the extent that the reflections may be completely lost. This likely indicates that there is too much Ge in the parent zeolite, a part of it is located in the layers, and the appropriate action in this case is to prepare a parent with less Ge content and repeat the protocol.

If the disassembly step appears to work successfully, tit might still be necessary to consider optimising the reaction conditions. At low acidity, all the interlayer species are removed from UTL but after an induction period atomic species are reintroduced between the layers (Figure 7), the length of the induction period depending on the conditions. However, at high acidity the removal of the species from between the layers may never be fully completed (Figure 8) before rearrangement leads to the formation of a stable precursor, usually analogous to IPC-2P. In other words, under concentrated acid conditions the rearrangement process becomes so fast that the induction period becomes zero and full disassembly to the layered IPC-1P precursor does not have time to occur before the reorganisation to IPC-2P takes place. With different parents this type of behaviour may occur at different conditions and so researchers should really test a good sample of conditions to make sure they do not miss potential ADOR products.

A question often asked is about the universality of the ADOR process. In our experience to date, all germanosilicate zeolites that have the requisite compositional and structural features can be disassembled, organised and reassembled into new zeolites. In that sense the ADOR process is perfectly universal given the limitations on chemistry and topology described. However, the key is to identify the right conditions – and this is where this protocol will find its most enduring impact.

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Author Contributions S.E.H completed the development of the protocol and collected the synthesis data. M.M. completed the electron microscopy, C.M.R., G.P.M.B. and S.E.A. collected the solid-state NMR data. P.S.W., J.Č. and R.E.M. initiated the project. All authors have checked the protocol and contributed to the writing of the paper.

Competing Interests

There are no competing interests in this work.

Additional Information

Supplementary information is available for this paper at ⋯

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Data Availability Data supporting this publication is available from the University of St Andrews **https://doi.org/10.17630/057e6e1d-cd0d-4f5c-b062-53a71f62d619** or from the corresponding author upon request.

FIGURES

Figure 1. A schematic diagram highlighting the four steps of the ADOR process. Initial d4r-containing parent zeolite **UTL** is broken down through hydrolysis, to make the layered intermediate IPC-1P. These layers are organised before the Si-O-Si bonds are reformed through calcination to form a reassembled material with a different structure from the original assembled parent. [I really like this figure. The only problem for me, is that I really struggle to read white text on any background colour. Could the boxes have coloured borders with black text on a white background inside?]

Figure 2. The experimental setup for the protocol. A three-neck round-bottom flask is fitted with a condenser and a thermometer (or thermocouple). The final neck is used to add the parent zeolite to the reaction mixture and to sample small amounts of product using a pipette. A Buchner funnel and flask is available for immediate filtration of the samples ready for PXRD and other characterisation methods.

Figure 3. Selected PXRD patterns collected at 1 hour, 2 hrs 30 min and 8 hours after the ADOR reaction has started (water as the hydrolysis medium, 100 °C). The inset shows how the position of the *200* reflection shifts with time. The colour coding is the same as that used in Figure 4.

Figure 4. A plot of the variation of d spacing of the *200* PXRD reflection versus time for the ADOR reaction carried out in water at 100 °C. The plot shows clearly the different regimes of the process. The disassembly of the parent Ge-**UTL** zeolite happens rapidly and is complete inside 1 hour. There follows an induction period where IPC-1P is the only identifiable product. Following this a new process occurs where the d-spacing increases, finally forming a different product, IPC-2P. The coloured symbols show the

samples whose full PXRD patterns are shown in Figure 3. The precision in the measurement of the PXRD d spacing is within the symbols on the diagram.

Figure 5. Extent of reaction, α, plotted against time. (a) Plot for the hydrolysis (D; left) and, (b) rearrangement (O; right) steps for the 100 ˚C reaction in water. Each plot was fitted with the Avrami-Erofeev model to find the Avrami exponent, n and the rate constant, k. In these examples, for the D step n = 0.36 and k = 1.36 min^{-1} and for the O step n = 3 and k = 0.0085 min^{-1}.

Figure 6. ^{29}Si (9.4 T, 10 kHz MAS) NMR spectra of calcined Ge-**UTL** parent zeolite, and subsequent hydrolysis after 1 hr, 4 hr and 8 hr. The change in intensity of Q^4 ($Si(OSi)_4$) and Q^3 ($Si(OSi)_3(OH)$) species is monitored over this time period.

Figure 7. Hydrolysis of Ge-**UTL** in water over a time period of 8 hr showing the d spacing, d_{200} for 100 °C (black), 92 °C (green), 85 °C (red), 81 °C (cyan), 77 °C (orange) and 70 °C (blue). After 1 hour at all temperatures Ge-**UTL** is hydrolysed to IPC-1P, which then rearranges to IPC-2P after an induction period that varies with temperature. The precision in the measurement of the PXRD d spacing is within the symbols on the diagram and highlighted by black error bars.

Figure 8. Hydrolysis (disassembly) of Ge-**UTL** over a time period of 8 hr showing the d_{200} spacing for reactions with 6 M (pink), 1.5 M (blue), and 0.1 M (green) hydrochloric acid at 20 °C. There is a significant difference between the reaction in 6 M HCl than for the others. This can be explained by understanding that increased acidity promotes the rate of the rearrangement reaction to such a degree that when 6M HCl is used the disassembly never reaches IPC-1P as the rearrangement to IPC-2P is complete before the dentercalation of all the d4r units from between the layers has finished. This indicates that pH can also be used to control the outcome of the ADOR process.

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